= EP 0 513 025

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : G01N 21/65, G07D 7/00 G02B 26/00

A1

(11) International Publication Number: WO 91/11703

(43) International Publication Date: 8 August 1991 (08.08.91)

(21) International Application Number: PCT/GB90/02032

(22) International Filing Date: 28 December 1990 (28.12.90)

(30) Priority data:
9002335.9 2 February 1990 (02.02.90) GB

(71) Applicant *(for all designated States except US)*: THE DE LA RUE COMPANY PLC [GB/GB]; De La Rue House, 3/5 Burlington Gardens, London W1A 1DL (GB).

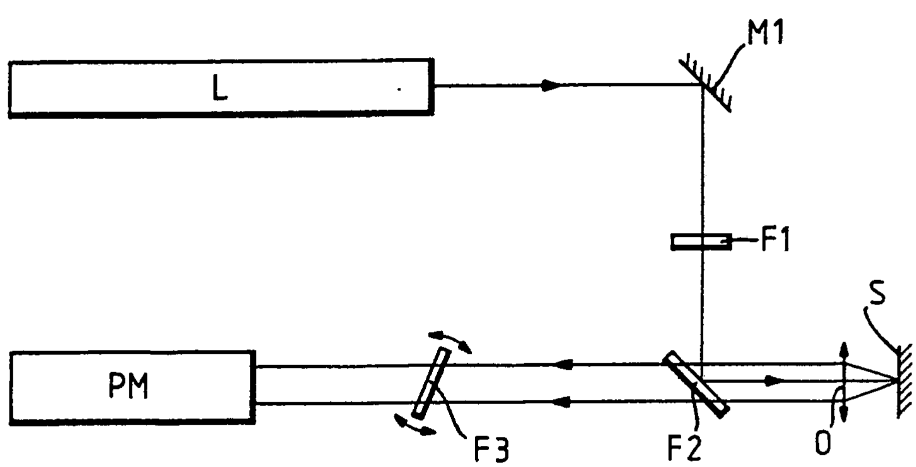
(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : BRATCHLEY, Robin [GB/GB]; 30 Bingley Grove, Woodley, Reading, Berkshire RG5 4TT (GB). BATCHELDER, David, Neville [GB/GB]; 16 Meynell Gardens, London E9 7AT (GB).

(74) Agent: DILL JENNINGS & EVERY; 53/64 Chancery Lane, London WC2A 1HN (GB).

(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB, GB (European patent), GR (European patent), IT (European patent), LU (European patent), NL (European patent), SE (European patent), US.

Published
With international search report.
With amended claims.

(54) Title: DETECTION APPARATUS



(57) Abstract

Apparatus that can be used to authenticate a security item or otherwise analyse a sample (S) containing a Raman-active material, comprises a substantially monochromatic light source (L); means (M1, F1, F2, O) for directing the source light onto the sample; means (F2) for separating the source light from the radiation emitted from and/or scattered by the sample; means adapted to discriminate (F3) between the Raman-scattered light and light of a neighbouring wavelength; and one or more deflectors (PM) for the respective discriminated radiations. The apparatus allows a distinction to be drawn between the Raman scattering and background fluorescence.

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DETECTION APPARATUS

Field of the Invention

This invention relates to apparatus suitable for detecting resonance Raman scattering. The apparatus is particularly useful for the authentication of appropriately marked security documents, for example in banknote-sorting equipment.

Background of the Invention

Security-printed or other authenticatable items such as banknotes, cheques, passports, licences and tickets need to be produced in a manner which allows genuine articles to be authenticated. The security printing industry has seen a wide variety of measures being adopted, ranging from easily-recognisable visual features through discrete visual features to machine-verifiable characteristics. As with the visual features, some machine-readable attributes may be relatively readily apparent, such as fluorescent features, while others may be more concealed, requiring specially made authenticating apparatus.

A security printer is able to select a variety of measures to prevent counterfeiting and forgery and to allow authentication. Any one document will include a range of them, and the choice of those that are actually included in any one document or part of a document presents a formidable obstacle to wrong-doers.

There is a constant need to add to the measures which are employed, particularly those which lend themselves to present-day security printing manufacturing equipment such as automatic banknote-sorting equipment.

The Raman spectra of chemical compounds have been used for many years as a means of identification. Raman spectra arise when laser light incident upon a sample of the material is scattered: the scattered light includes light of the laser wavelength plus, at much lower intensity, light of additional wavelengths which are characteristic of the compound. The additional light appears at frequencies

which are shifted from that of the laser beam by amounts equal to the frequencies of collective vibrations of the atoms in the compound. These frequencies are determined by the masses of the atoms comprising the material and the forces which hold them together. As these are almost always unique for every chemical compound, the Raman spectrum is often used as its fingerprint. In this way, the compound may be identified in various conditions, for example as a crystal, in solution, as a powder and in mixtures with other compounds.

Resonance Raman scattering (RRS) occurs when the wavelength of the incident laser beam is equal to, i.e. in resonance with, that of an optical absorption band in the material. The electrons responsible for the absorption are often located on a subset of atoms in the compound known as the chromophore. Under resonance conditions the Raman scattered light which is frequency shifted by the collective vibrations of atoms in the chromophore will be greatly enhanced in intensity.

In most respects, conventional Raman scattering spectroscopy provides information complementary to that obtained from infra-red absorption spectroscopy. As the instrumentation is usually considerably more expensive than that for a comparable infra-red apparatus, Raman spectroscopy has usually only been used when infra-red spectroscopy is incapable of providing required information. For example, conventional Raman spectroscopy requires lasers of high power (about 100-200 mw) and a sophisticated, sensitive spectrometer requiring cooled photomultipliers. The commercial application of such apparatus has historically been limited, owing to its high cost and large size.

Raman-active compounds are known, for example polydiacetylenes. Polydiacetylenes have a conjugated polymer backbone. Raman-active compounds, for the purposes of this specification, exhibit Resonance Raman activity or other Raman activity of similar intensity.

US-A-4586819 discloses a "laser Raman microprobe" that separates a laser beam reflected by a sample and Raman-scattered light generated by the sample, using a filter that transmits or reflects light in a predetermined wavelength region. All light transmitted at the Raman-scattering wavelength is subjected, via a single monochromator, to spectroanalysis.

Patent Abstracts of Japan (1988) 9(265) 399, discloses apparatus adapted to eliminate the influence of fluorescence when detecting wavelength-modulated Raman-scattered light. The apparatus involves a mechanically-complex oscillating slit arrangement which oscillates at a rate slower than the wavelength-modulated incident radiation.

Summary of the Invention

Novel apparatus that can be used for analysing a sample including a Raman-active material comprises a substantially monochromatic light source; means for directing light of the source wavelength onto the sample; means for collecting radiation emitted from and/or scattered by the sample, and means for separating the source light from the collected radiation; means adapted to discriminate between the Raman-scattered light and light of a neighbouring wavelength; and one or more detectors for the respective discriminated radiations.

The novel apparatus can be used to analyse security documents for the presence of a Raman-active compound, e.g. compounds and security documents of the types described and claimed in a copending International Application filed in the name of The De La Rue Company plc et al, having the same filing date, and entitled "Ink Compositions and Components Thereof".

Description of the Invention

Each of the components in apparatus according to the invention may be known, but their combination is novel and simple. The light source preferably provides intense monochromatic light, and is preferably a laser, and can be

a relatively inexpensive, low-power laser such as a HeNe laser. As is conventional, it may be combined with a filter which removes spurious laser radiation so that monochromatic light, e.g. at a wavelength of 632.8 nm, is passed. The source and/or the detector may be solid-state devices, so that the apparatus can be compact.

The selective transmission means is preferably a filter which, at the wavelength of the monochromatic source, allows the incoming beam to be reflected onto the sample and that portion of the beam scattered by the sample in the direction of the filter to be transmitted through it, to allow detection of the Raman-scattered light. In this case, light is incident on the sample at 90°, and scattered radiation can be processed along the same axis. Alternatively, the source light may be incident on the sample at another angle, and the scattered light may be processed along a different path from incidence. For a sufficiently thin sample, the scattered radiation-processing devices may be on the opposite side of the sample from the source.

The selective filter in apparatus according to the invention may also be of a known type, as may be the detector. As indicated below in connection with the drawings, a plurality of detectors may be used, e.g. to distinguish Raman scattering and fluorescence, but a single device may be employed, e.g. if the apparatus is to detect a known Raman-active compound for its presence on a security document.

In a preferred embodiment of the invention, the apparatus additionally comprises means adapted to split the transmitted Raman-scattered light and transmitted light of a neighbouring wavelength, detection means for each of the split radiations, and means for comparing the two beams. For example, a conventional beam-splitter which splits the transmitted light along two paths is associated with filters in each path, one filter passing essentially only Raman-scattered light and the other excluding Raman light

and passing longer (or shorter) wavelength light just clear of the Raman band. The filtered beams are compared, for the purposes of analysis.

In order that the novel apparatus should be particularly useful for the authentication of security documents, it should be able to discriminate between Raman and other emissions of the same wavelength.

The Stokes-type Raman scattering will usually be measured, as that signal will be at lower energy and longer wavelength, although it is possible to measure the anti-Stokes Raman scatter. The fluorescence from a sample can be measured in the same geometric arrangement as the Raman scatter. The fluorescence band will however be broad and smooth, unlike the Raman spikes. The novel apparatus can distinguish the two components. In use, the signal at the Raman frequency is measured and so also is a neighbouring background signal immediately beside the Raman spike. By subtraction, the value of the Raman spike is obtained, and this can be used for authentication. Possibly there may be some other scattering components in the neighbouring background apart from fluorescence, but it is unlikely that they will have spikes at the measured Raman wavelength.

The discrimination can be achieved in a number of ways. In one embodiment, i.e. in a "static" detector for use with stationary authenticatable items, a tunable filter is employed. Two neighbouring readings from the sample are made, with the filter respectively tuned on and just off the Raman peak, to distinguish the true Raman component.

Alternatively, a pair of filtered detectors can be employed, one measuring the Raman signal and the other the background. Narrow band-pass filters, monochromators or tunable filters may be used. A fixed arrangement of this type could be used in a "dynamic" detector where, say, banknotes have to be checked quickly. Such equipment can allow the authentication of documents moving at speeds of up to 10 metres per second.

In a further embodiment, modulating the source intensity can be used to provide comparative signals. The benefit of modulation is that the background illumination components can be removed, so allowing the system to be used in less dark conditions.

The two wavelengths measured can be determined from a knowledge of the Raman spectrum of the authenticatable working material. At one wavelength, there should be substantially no Raman scattering by comparison with the scattering at the other wavelength.

The invention will now be described by way of example only with reference to the accompanying drawings, in which:

Figures 1 to 4 are each schematic representations of different embodiments of apparatus according to the invention;

Figure 5 shows the spectral characteristics of a selective filter suitable for use in the invention;

Figures 6A, 6B, 7 and 8 show various resonance Raman spectra; and

Figure 9 is an oscilloscope trace.

In operation of the apparatus illustrated in Fig. 1, light of wavelength 632.8 nm from a 3-7 mW helium-neon laser L is deflected through 90° by a mirror M1. It then passes through filter F1 which removes spurious radiation from the laser beam, only passing, substantially monochromatic, the 632.8 nm line. Such a filter, passing essentially only 630-634 nm wavelength light, is available from Glen Spectra Ltd., Stanmore, Middlesex, England.

The laser light is then deflected by filter F2 through 90° so that it passes through a microscope objective O, by which it is focused on the sample S to be authenticated. Some of the light which is scattered by the sample is then collected by the microscope objective O and returns in the direction from which the laser beam came. The special features of filter F2 come into effect to segregate the Raman-scattered light from the much more intense, elastically-scattered light which has the same wavelength

as the laser light. While the light of wavelength 632.8 nm is again deflected through 90°, back towards the mirror M and the laser L, the Raman-scattered light (plus any fluorescence present) at longer wavelength passes straight through. While it is possible to use a 50:50 beam-splitter instead of filter F2, it is preferred to use a filter of the type having the spectral characteristics shown in Fig. 5, as available from Omega Optical Corp., USA.

Figure 5 shows the relationship between the percentage transmission value and the wavelength for a selective filter suitable for use in the invention. R_p and R_s represent the reference in the P and S planes of polarisation; F_p and F_s represent the filter in the P and S planes of polarisation. The spectra indicate a substantial drop in the percentage transmission value of the incident laser wavelength of 632.8 nm. This decrease corresponds to the passage of Raman-scattered light through the filter, and the deflection through 90° of the more intense, elastically-scattered light that has the same wavelength as that of the incident laser light. Hence very little light of wavelength 632.8 nm passes through the filter.

Spectral analysis of the Raman-scattered light, and its separation from the broad fluorescence, is carried out by a filter F3. Filter F3 functions to separate the scattered light into Raman emission and a neighbouring background signal. For a given source wavelength, and a particular Raman-active compound to be detected, the filter F3 may be a stationary filter having a characteristic pass-band for the Raman-scattered light. This is particularly appropriate if the fluorescence is wide-band. Alternatively, the filter F3 may be tunable, by rotation (see the arrows). Such a filter has special characteristics: when the light is perpendicular to the filter it has one characteristic pass-band; when the angle of the filter with respect to the light beam is decreased from 90°, however, the pass-band shifts to shorter

wavelengths. The equation which relates the wavelength of the centre of the pass-band, λ_c, to the angle, β, through which the filter F3 has been rotated from its position perpendicular to the light beam is:

$$\lambda_c = \lambda_{max} [1 - (0.47 \sin \beta)^2]^{1/2}$$

The filter F3 is suitably selected to cover the range from 701.6 nm at normal incidence to 692.2 nm at an angle of 20°. This is appropriate for Raman-scattered light on illumination of a Raman-active compound, of the type defined in the copending Application, in the vicinity of maximum absorbance, e.g. using laser light at 632 nm. Thus, the filter has a tuning range for the analysis of Raman-scattered light displaced to lower energy by 1357 cm^{-1} to 1550 cm^{-1}, in the central region of the Raman spectrum. Other filters can be used to obtain optimum results with different lasers and other Raman-active materials.

Finally, the light which passes through filter F3 is detected by a photomultiplier PM and its associated electronics. If desired, a chopper may be used to modulate the laser beam, so that phase-sensitive detection may be used. If the Raman-scattered light is sufficiently intense, however, e.g. if a polydiacetylene is being detected, simple DC detection is also appropriate.

In specific experimental investigations, a HeNe laser producing 3-7 mW of power at 632.8 nm was used. The polarisation of the beam was perpendicular to the plane of Figure 1, a requirement for the operation of the filter F2. The intensity of the laser beam at the sample, after having been reduced by the filters, was approximately 1.5 mW. The photomultiplier was a Thorn EMI 9658 operated at 900 V at room temperature. The DC output from the tube was measured using a digital voltmeter (DVM).

The rotation of the filter F3 was driven by a simple micrometer screw. In initial experiments, point-by-point measurements were made. To speed this procedure, a motor

drive was attached to the micrometer, with the output of the DVM connected to a chart recorder.

For most of the experiments, the microscope objective was an X40 with a numerical aperture of 0.65 and a working distance of only 0.7 mm. Alternatively, a long working distance X40 objective of numerical aperture 0.4 and working distance 7 mm may be used. A X10 objective with a numerical aperture of 0.25 and a working distance of 6.7 mm was also used successfully. The longer working distances are more suitable for use on banknote-sorting equipment.

The first measurements were carried out on single crystals of a polydiacetylene. Figure 6A is a plot of the photomultiplier output, equivalent to intensity, as a function of angle through which the filter F3 had been manually turned. At zero angle, filter F3 is perpendicular to the beam of scattered light. Figure 6B is a plot of the resonance Raman spectrum taken on a conventional Raman spectrometer. The agreement between the two is very good, providing allowance is made for the lower resolution of the filter and the fact that its transmission decreases with increasing angle. The intensity at the peak of the photomultiplier output corresponded to approx. 3 pW.

The intensity reaching the photomultiplier actually increased when the print samples containing microcrystals of polydiacetylene were investigated. Typically, the maximum intensity was 5 pW, although a greater percentage of this was fluorescence than in the case of the single crystal. Most of this fluorescence, as was known from the previous measurements, came from either the underlying paper or ink vehicle. In fact, for some of the samples, the presence of polydiacetylene in the ink served to reduce the amount of fluorescence output considerably.

For a spectrum as shown in Figure 6B, the Raman and background combined signal would conveniently be measured at 1500 cm^{-1}, and the background on its own at 1400 cm^{-1} or 1600 cm^{-1}. These constitute the neighbouring signals which are used for the determination of the net Raman signal strength.

Figure 7 shows the relative intensity of resonance Raman spectra for matching pairs of samples, one (21) using the ink vehicle alone, and the other (20) the polydiacetylene-loaded ink vehicle. The value of 1 on this relative scale corresponds approximately to 6 pW. The spectra were taken from the chart recording of the Digital Voltmeter output made as the micrometer was driven with a motor.

Figure 8 is a repeat spectrum of the sample in Figure 7, but taken using the X10 microscope objective. There are two important differences from the previous spectrum to note. Firstly, the intensity has decreased by about a factor of seven; this is to be expected as seven is approximately equal to the ratio of the squares of the numerical apertures of the two microscope objectives. Secondly, the resolution of the spectrum is considerably improved. This is due to the fact that it is easier to obtain a parallel output beam for the scattered light with the longer focal length lens. The pass-band of filter F3 is narrowest when the incident light is plane-parallel. It is clear that the reduction in intensity does not radically degrade the quality of the spectrum.

The spectrum in Figure 8 was taken with the sample at the optimum working distance of 6.7 mm. When the working distance was increased or decreased by 1 mm from that value, the intensities were decreased by about a factor of two, but otherwise the spectra were essentially unaffected.

In order to test the response time of the system, the filter F3 was adjusted to give peak intensity for the polydiacetylene polymer sample of Fig. 6A/6B, with no pigment (see Figure 7). A 500 Hz chopper was then used to modulate the laser beam. The oscilloscope trace of the resulting output is shown in Figure 9. The signal goes negative from 0 V and reaches a maximum peak-to-peak amplitude of 4 V. The 1 Megohm input impedance of the oscilloscope was the effective load resistor for the photomultiplier current. The period of the signal is 2 ms

and the signal can be seen to approach its maximum value in 1 ms. The spectrum is sufficiently noise-free to judge that a measurement could satisfactorily be made in this time.

The experimental results clearly show that clear, identifiable resonance-Raman spectra can be obtained from samples of paper printed with polydiacetylene-loaded inks. The time required for measurement was 1 ms or less. If the sample were passing the focal spot at 1 m/s, then a line 1 mm wide should be sufficient for identification.

Resonance Raman spectra of plain and UV bright paper were compared: there was very little difference in the fluorescence output of the two papers when the HeNe laser was used for illumination.

With a X10 (i.e. ten times magnification) microscope objective, it was found that a working distance of 6.7 mm was adequate. Within ±1 mm of the value, the spectra were acceptable. The X40 (0.65 numerical aperture) microscope objective collected seven times as much light, but its 0.7 mm working distance would usually require a contact head to be used. Alternatively, to overcome the requirement for using a contact head, a long working distance objective (e.g. 7 mm working distance) can be used.

Figure 2 is a schematic diagram of a further possible arrangement of optical components in an instrument. Beam-splitter BS1 is equivalent to F2 in Figure 1, and a 50:50 beam-splitter BS2 has been added. BS2 splits the transmitted light which thus takes paths P_1 and P_2. Fixed filters F2 and F3 have narrow (approximately 6 nm) pass bands selected so that F2 is centred on the wavelength of the main Raman band and F3 is centred at a longer wavelength just clear of that band.

Light in path P_1 passes through filter F2 to photomultiplier PM2; path P_2 is via mirror M2 and filter F3 to photomultiplier PM1. The instrument is set up so that outputs from the photomultipliers PM1 and PM2 are equal if equally illuminated by white light, i.e. light which has

uniform intensity over the spectral region covered by F2 and F3. This may be achieved by adjusting photomultiplier voltages. It is also necessary to keep within the operating range of the photomultipliers, so that the output is linear. When a polyacetylene sample or a security item including a printed or other genuine security-marked area is placed under the objective O at position S, photomultiplier PM2 will give a greater signal than photomultiplier PM1. Positive identification can then be rapidly made (in times of less than one msec) by the appropriate electronic circuitry.

The effect can be demonstrated by subtracting the output of one photomultiplier from the other using a differential oscilloscope. In practice, the difference in signal would allow differentiation of genuine articles relative to forgeries: as the acceptable levels of variation of Raman response would be known, the circuitry would regard articles as having passed the test or failed it.

The signals from the two photomultipliers can be electronically processed so that an analogue or digital status signal is produced, to indicate the presence or absence of a specific Raman-active material. In practice, the equipment will be calibrated so that a pass signal is produced if the signal from photomultiplier PM2 is above the level of that from photomultiplier PM1 by a predetermined amount. Otherwise a fail signal will be produced. If necessary, a marginal signal can be produced by appropriate circuitry.

The status signal produced from the above Raman limit test, can be used to drive other circuits, e.g. a lamp or visual indicator to indicate if the document is "genuine", "false" or, if required, "marginal". Alternatively, it could be used to operate on accept/reject mechanism in a wide range of document or currency handling equipment, e.g. money-acceptor, ticket-operated gate, bank card-reader, etc.

The response time of the Raman detector is sufficiently fast that it can be used in document sorting and verification equipment, especially for banknotes, tickets, passports, cheques, travellers' cheques, etc. In such cases, the genuine documents bearing the Raman-active material and passing the test would be authenticated by the equipment. Otherwise the document would be redirected by the equipment and collected separately as a suspect document.

In addition to checking authenticity, the equipment could also be used to read bar codes or other types of printed codes on documents which contain Raman-active compounds such as polydiacetylenes or diamond. For example, such codes could be used to discriminate between different denominations of banknotes.

By using a multiplicity of different units of the types shown in Fig. 2, it is possible to detect inks which contain Raman-active material which scatter at different wavelengths. This would markedly enhance the confidence and authenticity of such documents. Instead of a multiplicity of detectors, the optical path could be split after filter F2, by inclusion of appropriate beam-splitters, filters and additional photomultipliers, so that Raman-active materials scattering at different wavelengths could be simultaneously detected.

An alternative detector design for use in both static and dynamic detection modes is shown in Fig. 3.

Fig. 3 shows an arrangement similar to that of Fig. 2, except that a signal generator is connected to an acousto-optic modulator AO. This allows the laser beam to be modulated, turning the beam on and off at a frequency within the range 10 kHz to 1 MHz. For a corresponding "static" detector, the modulation frequency might be 500 Hz, but up to 100 kHz or higher is feasible for a dynamic mode, depending on the monitoring speed (e.g. 1 mm line of print at 1 m/sec). Part of the output from the signal generator is also connected to a phase-sensitive detector

which also receives the output signals from the photomultiplier detectors. The design has the same advantage as the apparatus of Fig. 2, in that the presence of fluorescence can be eliminated. The resultant signal which is free from background light interference can then be passed to a display device such as an oscilloscope (shown) or other discriminator.

An alternative use of an acousto-optic modulator AO is shown in Figure 4. In this design, the acoustic-optic modulator is modulated at a suitable frequency, e.g. 10 KHz. The modulator alternately passes light along paths P_1 and P_2. In the deflected path P_2, light is reflected from mirror M and passes through filter F1 at an angle. Filter F1 is of a similar type to F3 in Fig. 1, and the wavelength of transmitted light is dependent on angle. Path P_2 is for the shorter wavelength in Fig. 3, i.e. path P_2 is for the Raman frequency and path P_1 for the background (at longer wavelength).

If the correct Raman signal enters the detector, the photomultiplier produces a signal approaching a square wave. If a Raman signal is absent, both paths will produce the same signal at the photomultiplier, P_1 and P_2 being correctly balanced.

By appropriate electronic circuitry, the level of the AC signal produced can be used to provide a "Raman Limit Test" for subsequent use with authentication reading and sorting equipment.

An advantage of apparatus of the type shown in Fig. 4 is that effects due to the presence of fluorescence (which will be present in approximately equal amounts in P_1 and P_2) can largely be eliminated instantly. A further advantage of the apparatus shown in Fig. 4 over these shown in Figs. 2 and 3 is that only one filter and one photomultiplying detector are required.

Apparatus of the invention may be solid-state. A suitable arrangement would be similar to that shown in Fig. 3, except that the plasma rejection filter F1 used in Fig.

3 is not needed. In the solid state, operation may be in AC (modulated) or DC mode. However, the solid-state laser can be modulated electronically (e.g. in range 10-100 MHz) and an acousto-optic coupler is not needed. In DC mode, the operation of the instrument can be observed using an oscilloscope with differential inputs. In AC mode, a phase-sensitive detector is employed.

The laser wavelength of solid-state lasers typically falls between 670 and 675 nm. Solid-state photodetectors are exemplified by two types: silicon photodiodes and silicon photoavalanche diodes.

Raman-detectable materials may be included in items and documents to be authenticated in different places. In the case of documents, the material may be located on the same side or opposite sides of the document. The placing of the feature may be varied within the limits that a given detector system may allow.

Security document automatic sorting equipment incorporating the apparatus of the invention will generally also comprise:

(a) a hopper for holding multiples of documents to be verified;

(b) means for selecting from the hopper a document to be verified;

(c) means for transporting the document to and through the authentication equipment;

(d) means for receiving multiples of the documents which have been verified; and

(e) means for receiving, and optionally marking or spoiling notes which have not been identified as verified.

In another embodiment, a simpler automatic feeding device would enable one manually-sorted document to be scanned at a time. Such a device may comprise authentication apparatus of the invention and document-acceptor and document-expelling driving means and an electronic signalling means to indicate, visually, aurally or otherwise, whether a document has passed or not.

The apparatus of the invention is used for detecting the presence of Raman-active compounds which are on or near the surface of the item to be authenticated. The presence of Raman-active compounds may be detected within the body of such items, provided that the illuminating light can substantially reach the Raman-active compound, and that the resulting Raman and scattered light can be collected for analysis.

The apparatus may be used to authenticate items of any suitable kind including tagging and labelling markings, but is principally intended for use with security-printed items including security-printed documents. In general, therefore, the method of the invention is applicable to the analysis of any authenticatable item, of which security-printed items and security documents are examples, for the presence of a Raman-active compound.

CLAIMS

1. Apparatus for analysing a sample including a Raman-active compound, comprising a substantially monochromatic light source; means for directing such monochromatic light and means for collecting scattered light from the sample; means for discriminating between Raman and other transmitted scattered light emissions; and a detector for the discriminated emissions.

2. Apparatus according to claim 1, wherein the discrimination means comprises a tunable filter.

3. Apparatus according to claim 1, wherein the discrimination means is adapted to split the transmitted scattered light into Raman resonance emission and a neighbouring background signal, and the detector comprises means for detecting each of the two beams thus split and a comparator.

4. Apparatus according to claim 3, wherein the discrimination means comprises a tunable filter, narrow band-pass filter or monochromator.

5. Apparatus according to any preceding claim, wherein the light source comprises a laser.

6. Apparatus according to claim 5, wherein the laser is a HeNe laser.

7. Apparatus according to any preceding claim, wherein either or each of the source and the detector is a solid state device.

8. Apparatus according to claim 1, wherein the directing and collecting means comprise a filter which can reflect light from the source on to the sample and transmit scattered light from the sample.

9. A method of analysing a security document for the presence of a Raman-active compound, which comprises operating apparatus according to any preceding claim such that light from the source is focused on the document.

10. A method of authenticating banknotes, or sorting used banknotes, which comprises operating apparatus according to

any of claims 1 to 8, and selecting those banknotes which contain a Raman-active compound detected at a given wavelength.

AMENDED CLAIMS

[received by the International on 9 July 1991 (09.07.91) ; original claims 1, 3, 7 and 8 amended;other claims unchanged (2 pages)]

1. Apparatus for analysing a sample including a Raman-active compound, comprising a substantially monochromatic light source; means for directing light of the source wavelength onto the sample; means for collecting radiation emitted from and/or scattered by the sample, and means for separating the source light from the collected radiation; means adapted to discriminate between the Raman-scattered light and light of a neighbouring wavelength; and one or more detectors for the respective discriminated radiations.

2. Apparatus according to claim 1, wherein the discrimination means comprises a tunable filter.

3. Apparatus according to claim 1, wherein the discrimination means is adapted to split the emitted and/or scattered light and the light of a neighbouring wavelength, and the one or more detectors comprise means for detecting each of the two beams thus split and a comparator.

4. Apparatus according to claim 3, wherein the discrimination means comprises a tunable filter, narrow band-pass filter or monochromator.

5. Apparatus according to any preceding claim, wherein the light source comprises a laser.

6. Apparatus according to claim 5, wherein the laser is a HeNe laser.

7. Apparatus according to any preceding claim, wherein either or each of the source and the detector is a solid state device.

8. Apparatus according to any preceding claim, wherein the directing and collecting/separating means comprise a filter which can reflect light from the source onto the sample and transmit scattered light from the sample.

9. A method of analysing a security document for the presence of a Raman-active compound, which comprises operating apparatus according to any preceding claim such that light from the source is focused on the document.

10. A method of authenticating banknotes, or sorting used banknotes, which comprises operating apparatus according to any of claims 1 to 8, and selecting those banknotes which contain a Raman-active compound detected at a given wavelength.

Fig.1.

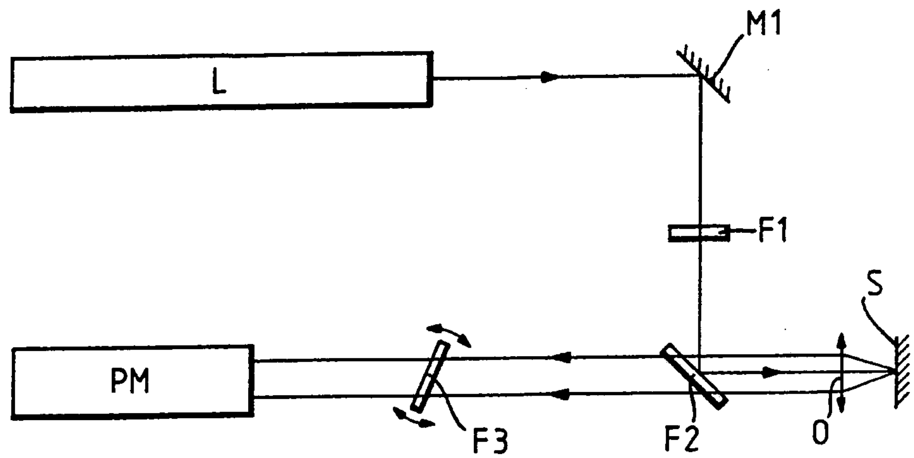

L
M1
F1
S
PM
F3
F2
0

Fig.2.

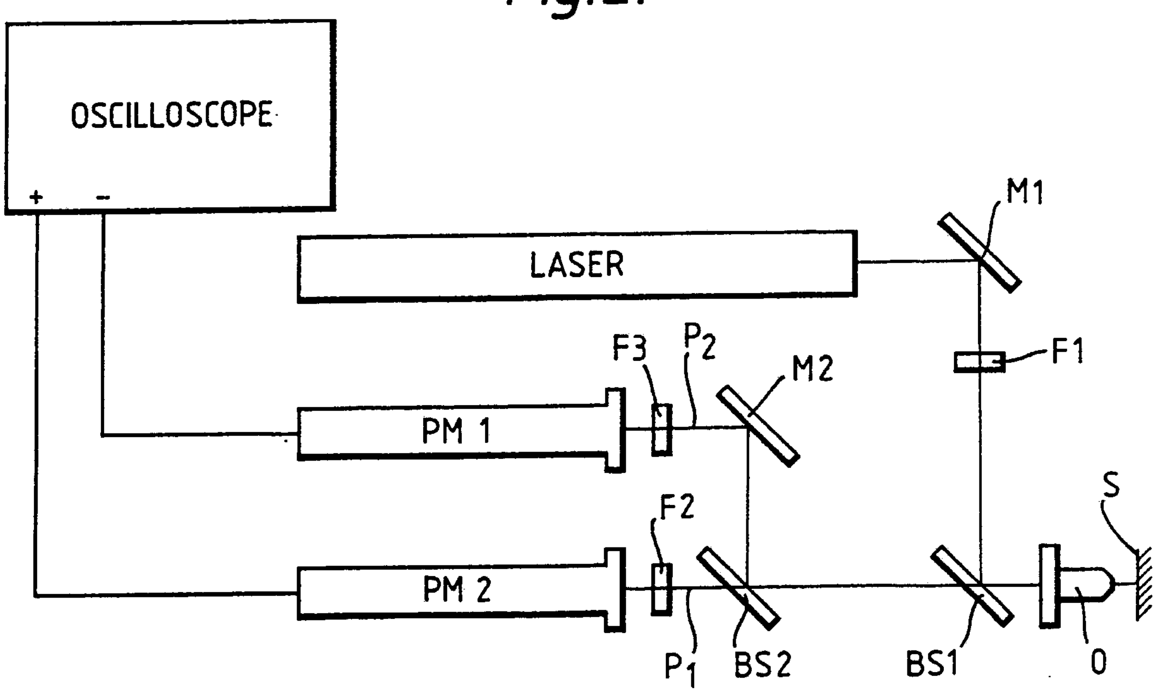

OSCILLOSCOPE
+
−
M1
LASER
F3
P2
M2
F1
PM 1
F2
S
PM 2
P1
BS2
BS1
0

Fig.3.

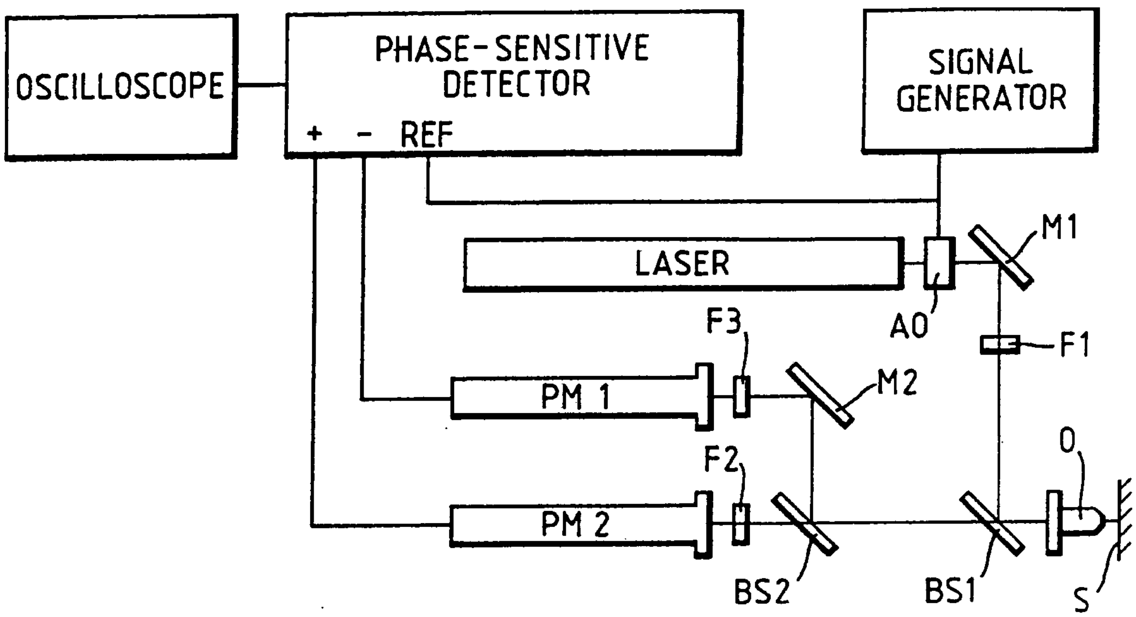

OSCILLOSCOPE
PHASE-SENSITIVE DETECTOR
+ - REF
SIGNAL GENERATOR
LASER
M1
AO
F1
F3
M2
PM 1
F2
O
PM 2
BS2
BS1
S

Fig.4.

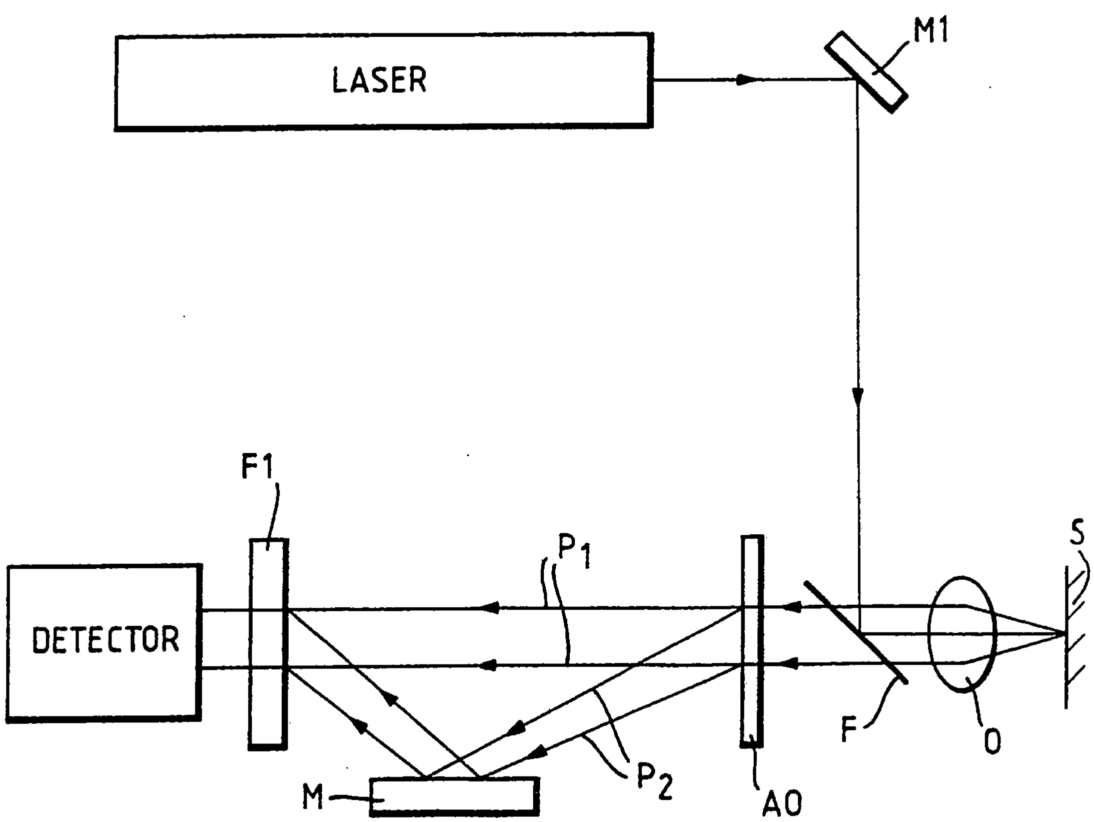

LASER
M1
F1
P_1
S
DETECTOR
F
O
P_2
M
AO

Fig. 5.

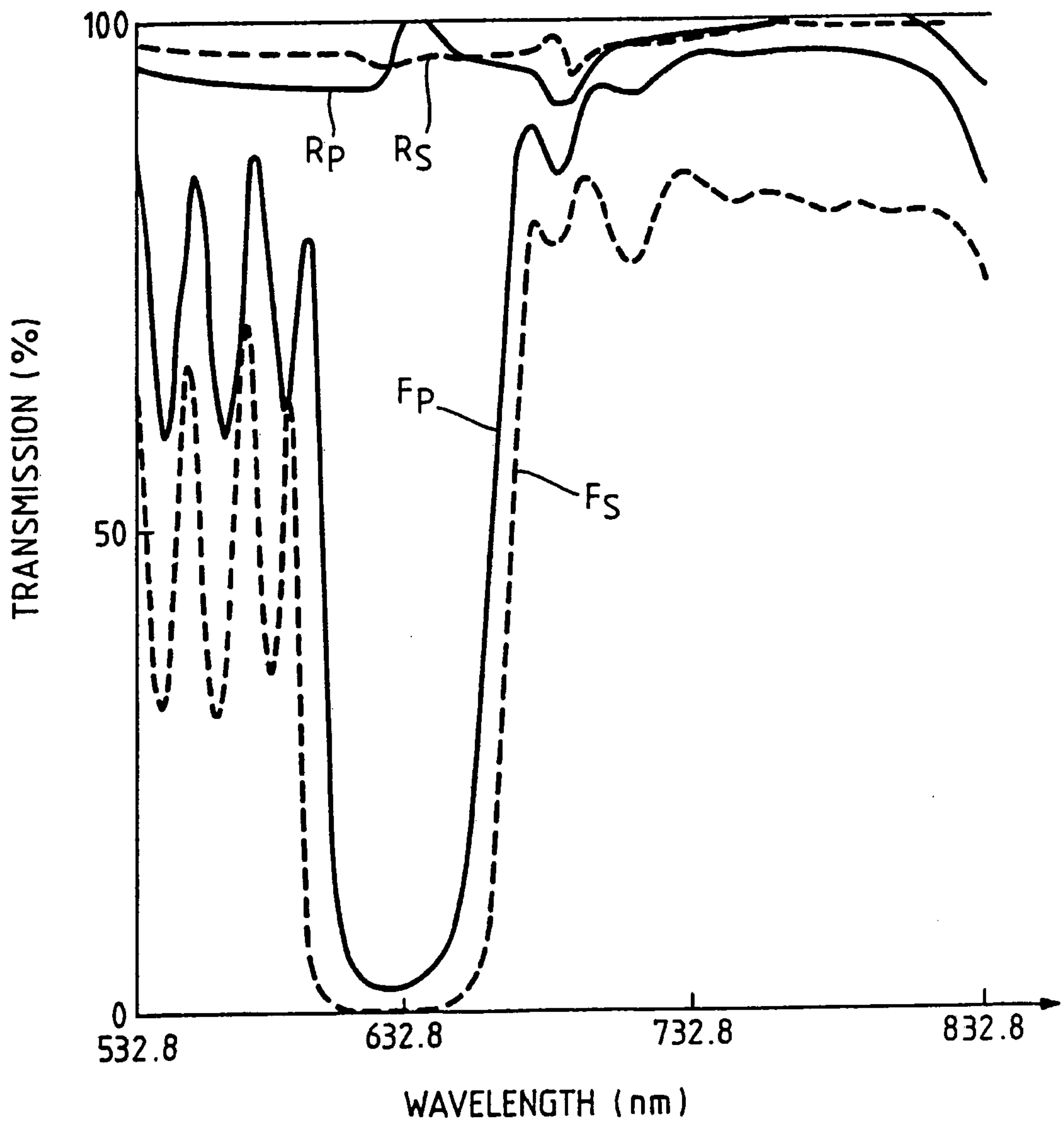

100
50
0
TRANSMISSION (%)
RP
RS
FP
FS
532.8
632.8
732.8
832.8
WAVELENGTH (nm)

Fig.6A.

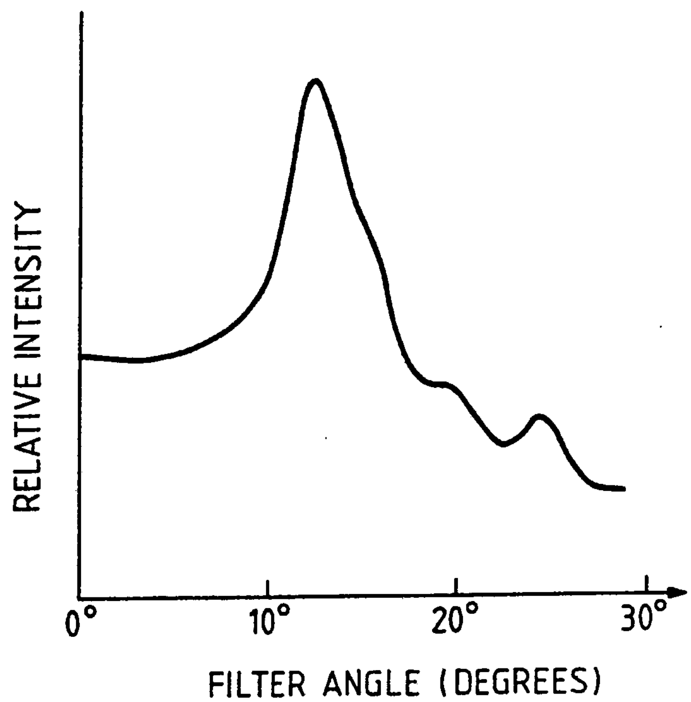

RELATIVE INTENSITY
0°
10°
20°
30°
FILTER ANGLE (DEGREES)

Fig.6B.

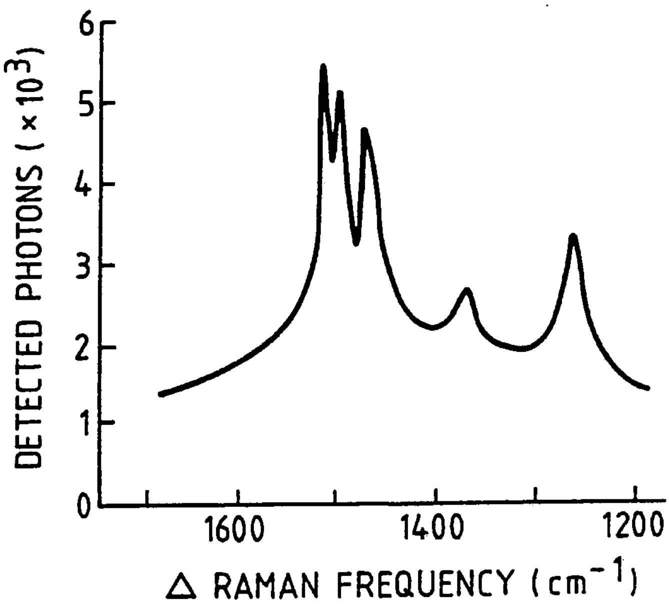

DETECTED PHOTONS (× 10^3)
0
1
2
3
4
5
6
1600
1400
1200
△ RAMAN FREQUENCY (cm^{-1})

Fig. 7.

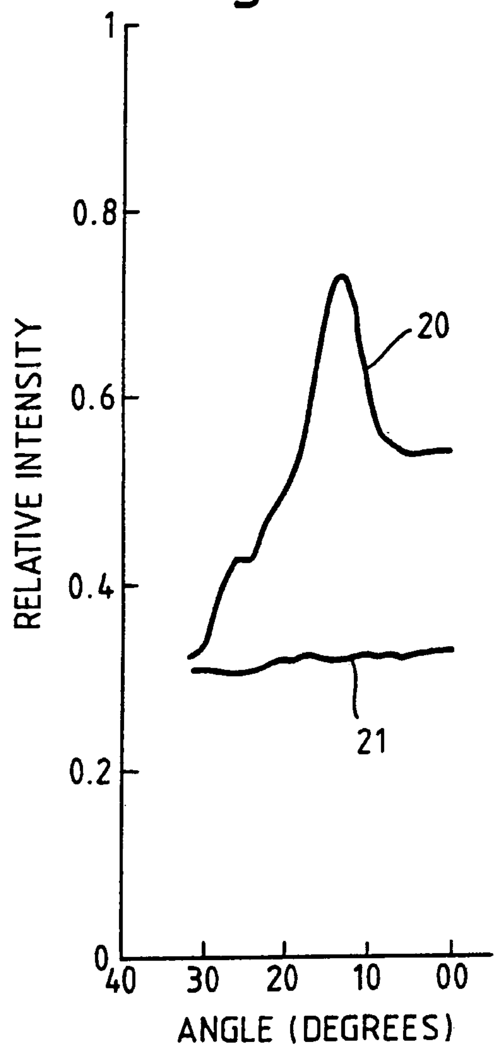


Fig. 8.

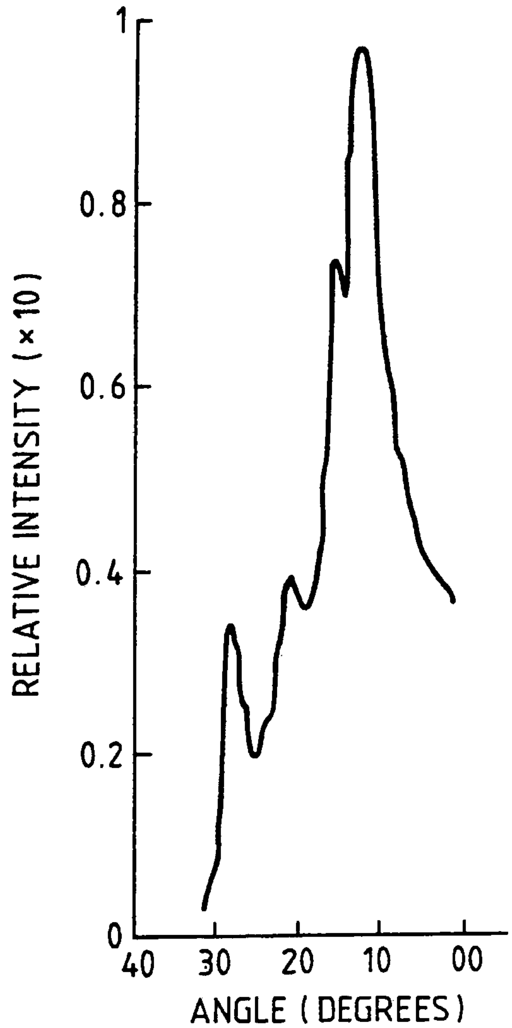
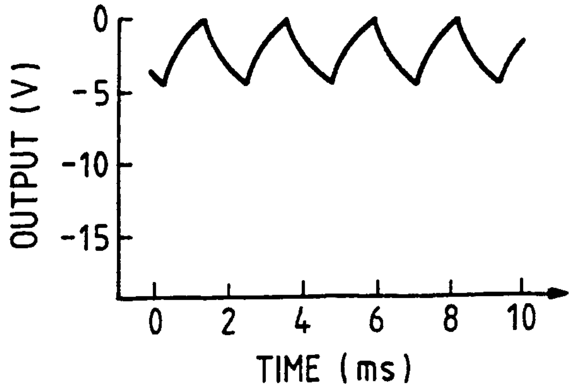


Fig. 9.



INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/02032

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: G 01 N 21/65, G 07 D 7/00, G 02 B 26/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC^5	G 01 N, G 07 D, G 02 B, G 01 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[*]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4586819 (TOCHIGI et al.) 6 May 1986 see figure 1; column 2, lines 16-67; column 3, lines 61-68	1,5,6,8
	--	
X	Patent Abstracts of Japan, vol. 9, no. 265 (P-399)(1988), 23 October 1985, & JP, A, 60113132 (KOGYO GIJUTSUIN (JAPAN)) 19 June 1985 see the abstract (cited in the application)	1,3-6
Y		2,4
	--	
Y	WO, A, 8801730 (THE AUSTRALIAN NATIONAL UNIVERSITY) 10 March 1988 see figures 1,4; page 1, paragraph 1; page 5, paragraph 2; page 7, paragraph 2	2,4
A		9,10
	-- ./.	

[*] Special categories of cited documents:[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12th April 1991	24.05.91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	miss T. MORTENSEN

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP, A, 0314312 (DE LA RUE SYSTEMS) 3 May 1989 see page 1, lines 2-5,23-26	7,9,10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9002032

SA 43289

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 29/04/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4586819	06-05-86	JP-A- 59010834	20-01-84
		JP-A- 59065242	13-04-84
		JP-A- 59107243	21-06-84
		FR-A,B 2530024	13-01-84
WO-A- 8801730	10-03-88	AU-B- 585466	15-06-89
		AU-A- 7918487	24-03-88
		EP-A- 0278976	24-08-88
		JP-T- 1501175	20-04-89
EP-A- 0314312	03-05-89	JP-A- 1141338	02-06-89
		US-A- 4935628	19-06-90